

Characterization of Ambient Air PM_{2.5} in the Pittsburgh Region



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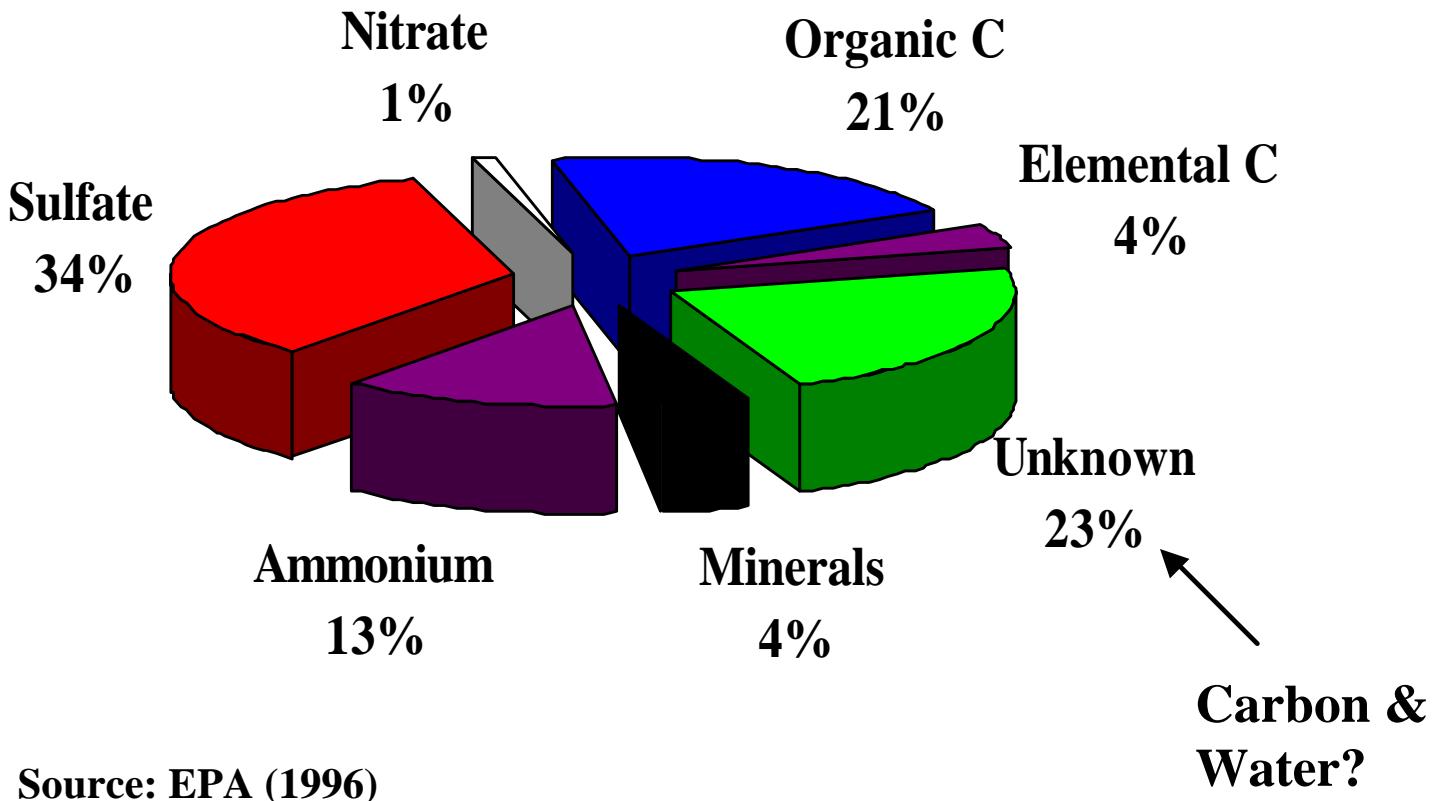
Why Is DOE Concerned About PM_{2.5}?

- Coal-based power systems contribute to PM_{2.5}
 - Primary particles
 - Ultra-fine fly-ash (Spherical Alumino-silicates,SAS), carbon soot
 - Gaseous precursors
 - SO₂, SO₃, NO_x
 - React with NH₃ in the atmosphere to form ammonium sulfate and ammonium nitrate particles
- SIPs will likely restrict emissions from coal power plants



Eastern PM_{2.5} Mass Apportionment

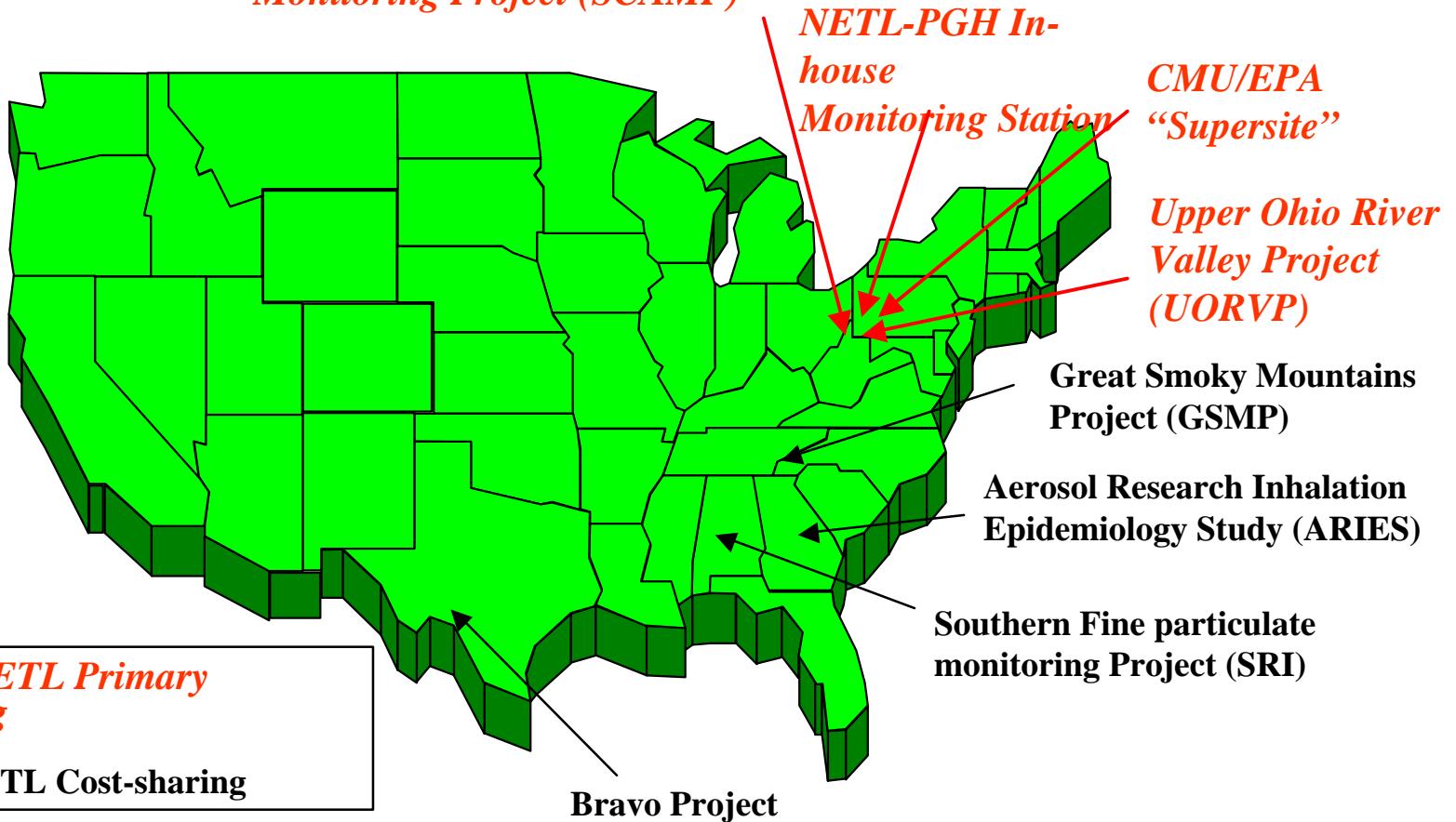
Current Understanding?



Ambient Sampling and Analysis

Current Project Portfolio

Stuebenville Comprehensive Air Monitoring Project (SCAMP)



Project Task Objective

- Measure the degree that coal-fired utilities contribute to the primary fine-particulate matter load in ambient air.

Experimental Approach

- Use Spherical Alumino-Silicates (SAS) as one measure of coal-fired utilities' contribution to the primary fine-particulate matter load in ambient air.



Experimental Objectives

- Quantitatively validate the SEM methods.
 - Assess comparability of polycarbonate filters to FRM teflon filters.
- Improve methods to account for most particle species on filters.
 - Identify particle species including SAS, sulfates, and carbonaceous.



Experimental – Sample Collection

- Andersen RAAS[®] 400 Speciation Sampler
- Four flow channels
 - One 16.7 L/m, teflon filter for FRM comparison
 - Two 7 L/m, polycarbonate filters for SEM
 - One 16.7 L/m, ‘quartz’ filter for EC/OC



Experimental – Sample Collection

- Channel configurations
 - 1: FRM teflon filter
 - 2: Carbon denuder, Pd coated polycarbonate filter, Nylasorb[®] filter
 - 3: Carbon denuder, uncoated polycarbonate filter, Nylasorb[®] filter
 - 4: Carbon denuder, ‘quartz’ filter, carbon filter



Experimental – Sample Collection

- Pre-weigh and post-weigh filters.
- Sample SEM flow channels at 7 L/m found to produce good particle dispersion at typical $15\mu\text{g}/\text{m}^3$ ambient air loading.
- Sample ambient air for 24 hours.
- Analyze SEM filters ASAP after sampling or store particle filters under controlled conditions.



Comparison of Gravimetric Filter Loading Variation:

**RAAS Polycarbonate versus FRM and
RAAS Teflon versus FRM**

Filter Type	Number of Filters	Avg. abs. difference,%	Standard Deviation
Polycarbonate	46	9.6	6.8
Teflon	163	5.6	6.8

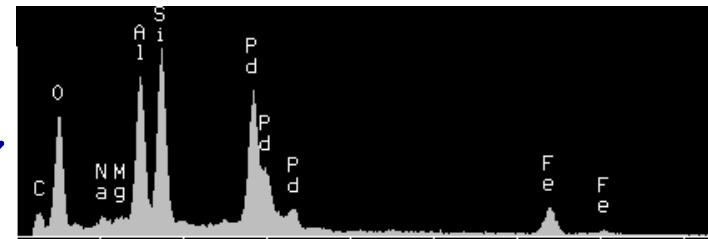
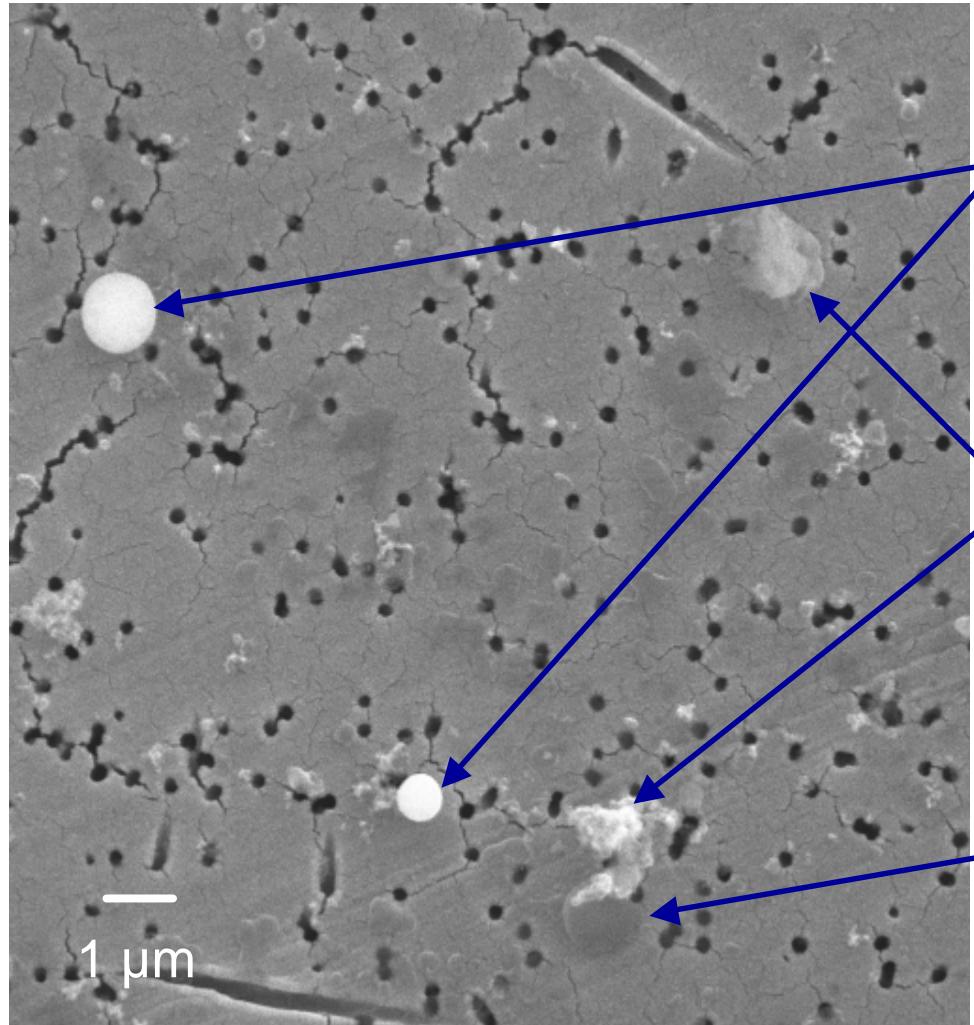


Scanning Electron Microscopy (SEM)

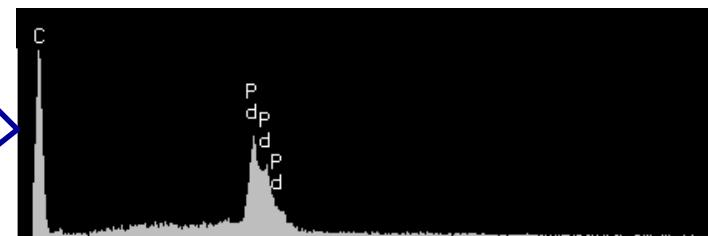
- SEM analysis can provide both morphology, size distributions, and elemental chemistry information for particle species determination.



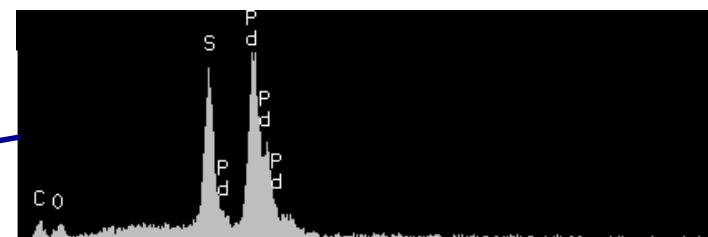
Secondary Electron Image



SAS Particle

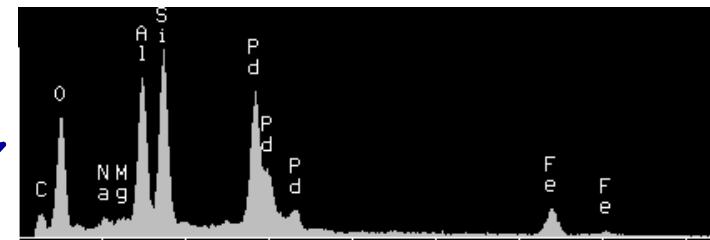
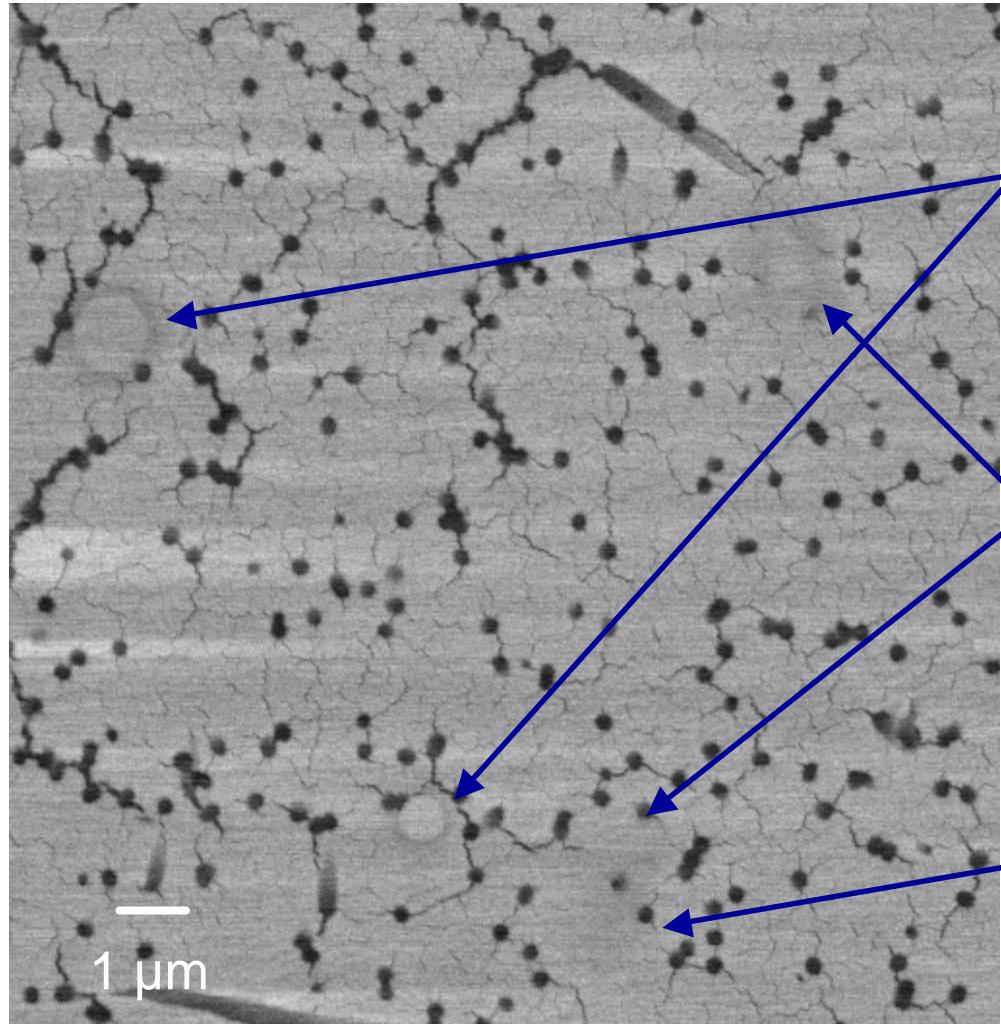


Carbon-rich Particle

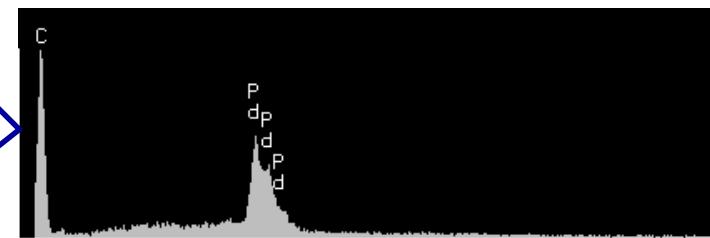


Sulfur Droplet

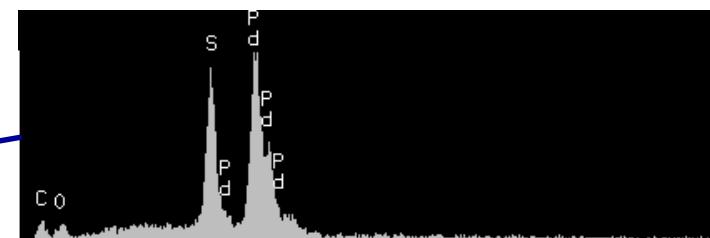
Backscattered Electron Image



SAS Particle



Carbon-rich Particle



Sulfur Droplet

Scanning Electron Microscopy (SEM)

- **Image information**
 - Secondary Electron (SE): Morphology & Size Distributions
 - Backscattered Electron (BSE): Chemistry, Morphology
- **Composition information**
 - X-ray (EDX/EDS): Chemistry



Experimental – SEM Analysis

- 15kV, stable beam current, fixed WD
- Reference spectra used, 7 sec spectra acquisition
- Mount filters with double sided silver tape
- SE image fields at 1000x, center to perimeter of filter wedge analyzed, particle ID threshold monitored
- Pd coated filters for carbon particle identification
 - C:Pd EDX ratio used for particle threshold



Comparison of Filter Area required to obtain 1000 Particle Images from filter Center and filter Perimeter

Section Location	Edge of filter	Tip of filter
Area Analyzed	0.0234 mm^2	0.0288 mm^2



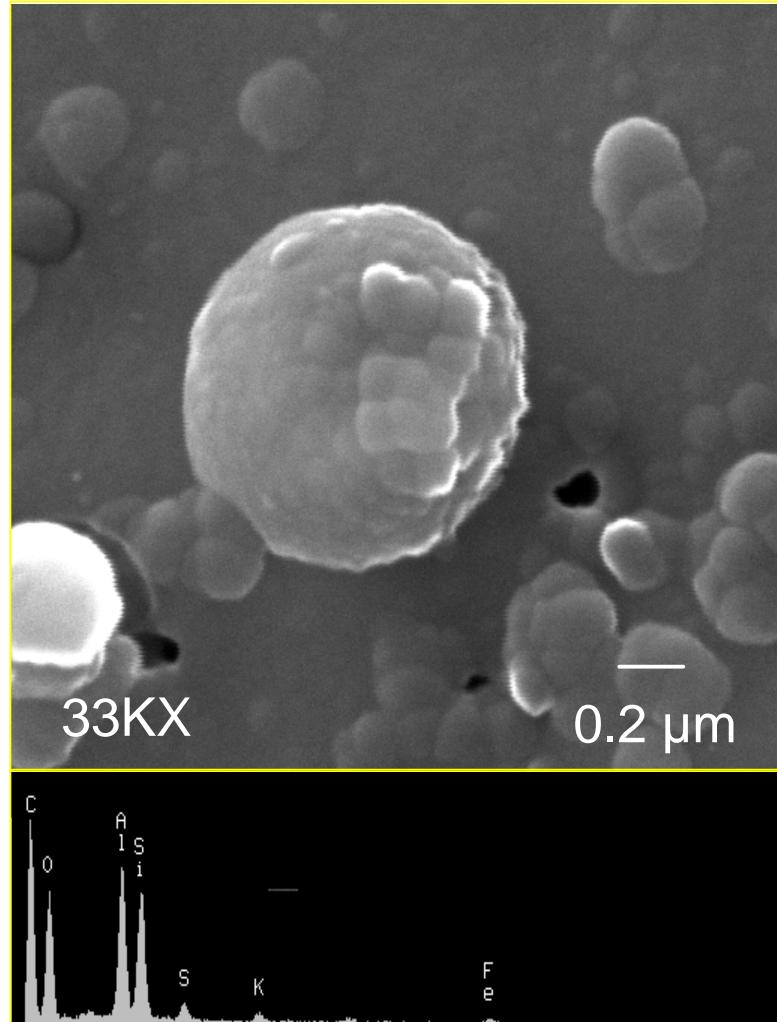
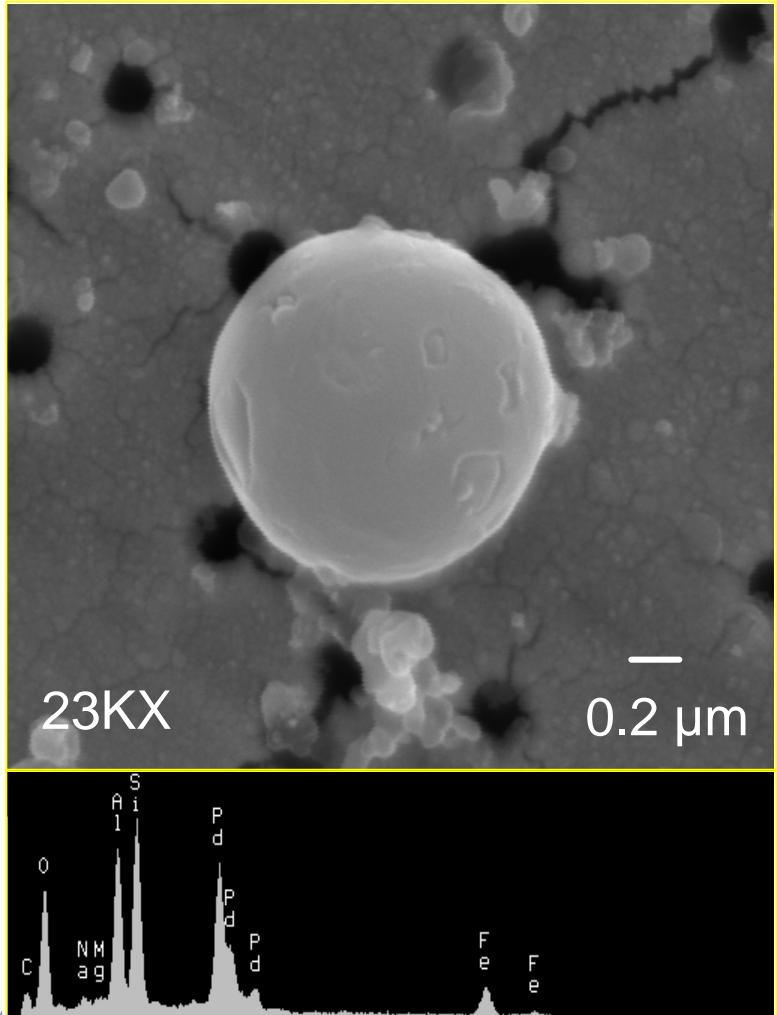
Comparison of Particle Species from filter Center and filter Perimeter, Excluding Ammonium Sulfate “Blobs”

Particle Type	Perim.	Center	Perim.	Center
	Number	Number	Weight	Weight
	%	%	%	%
SAS	1.8	1.4	4.1	4.3
C-rich	85.5	79.6	69.7	68.8
Crustal	8.6	14.4	21.3	23.8
S-rich	4.1	4.6	4.9	3.1



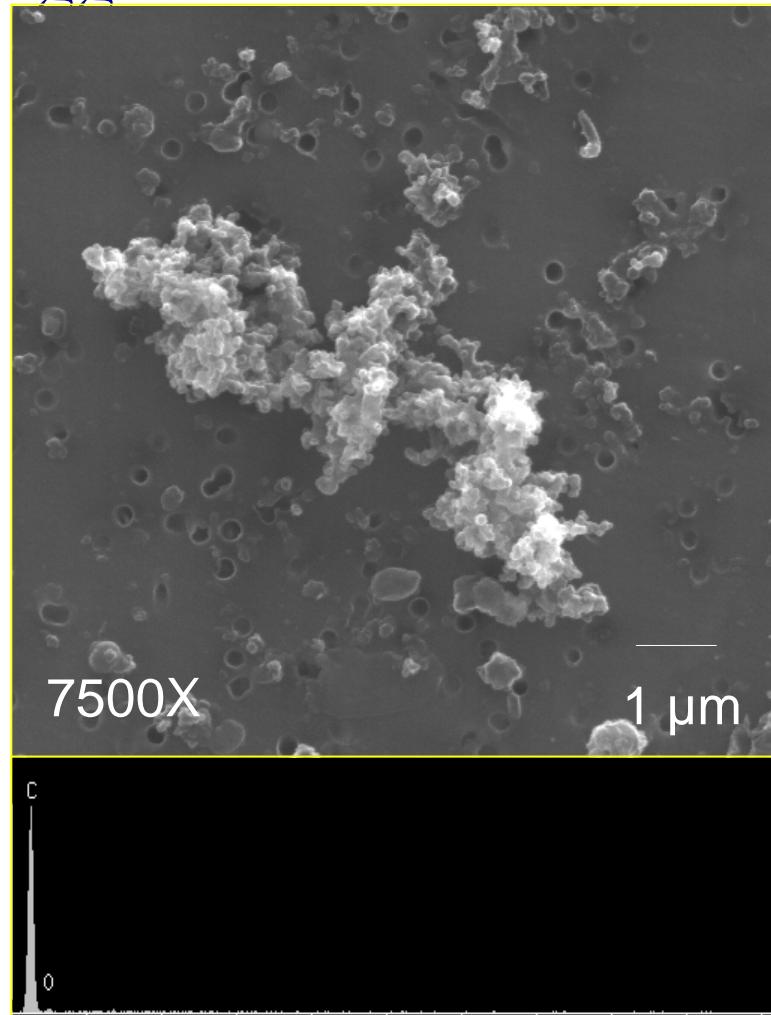
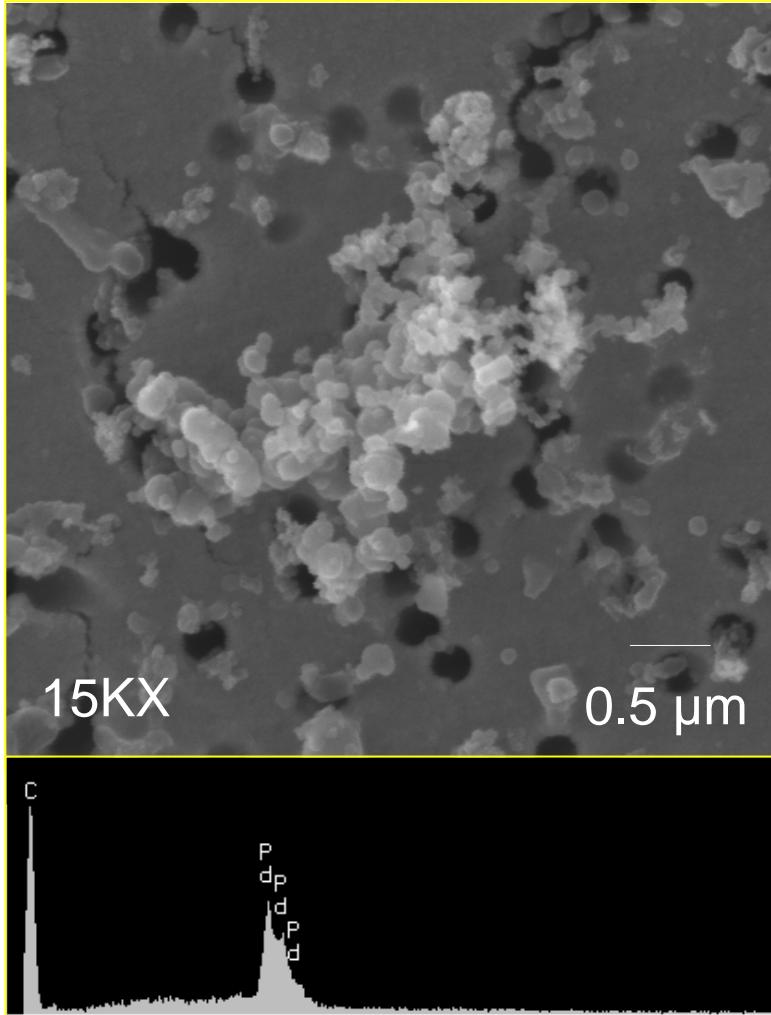
Secondary Electron Images

SAS



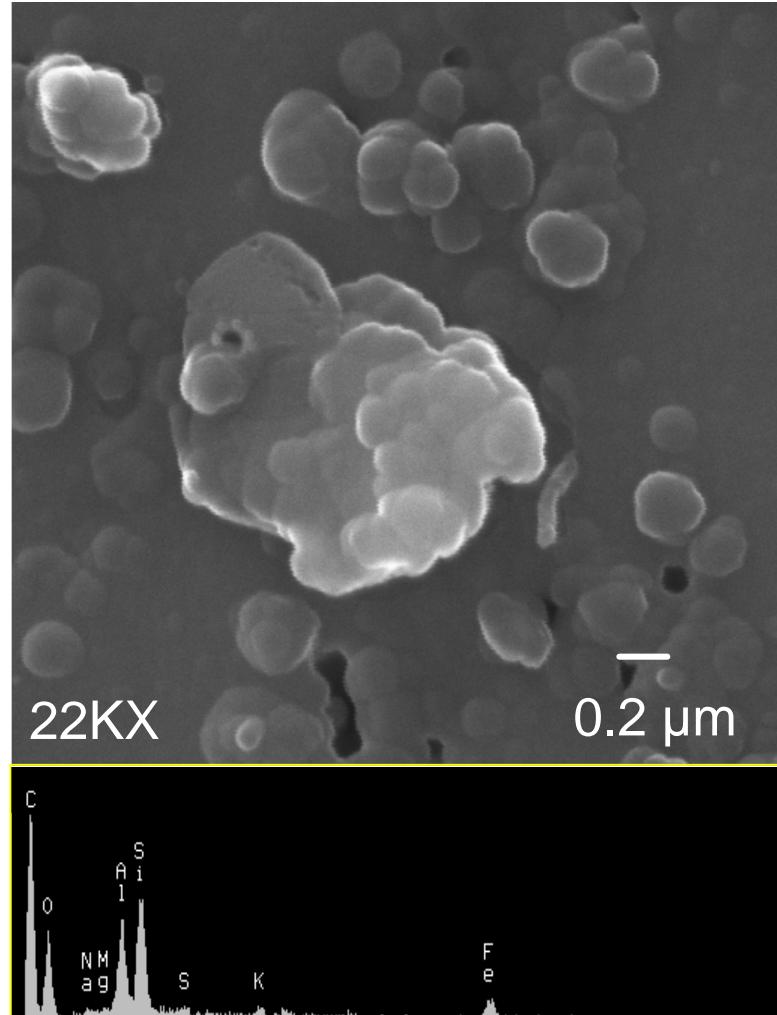
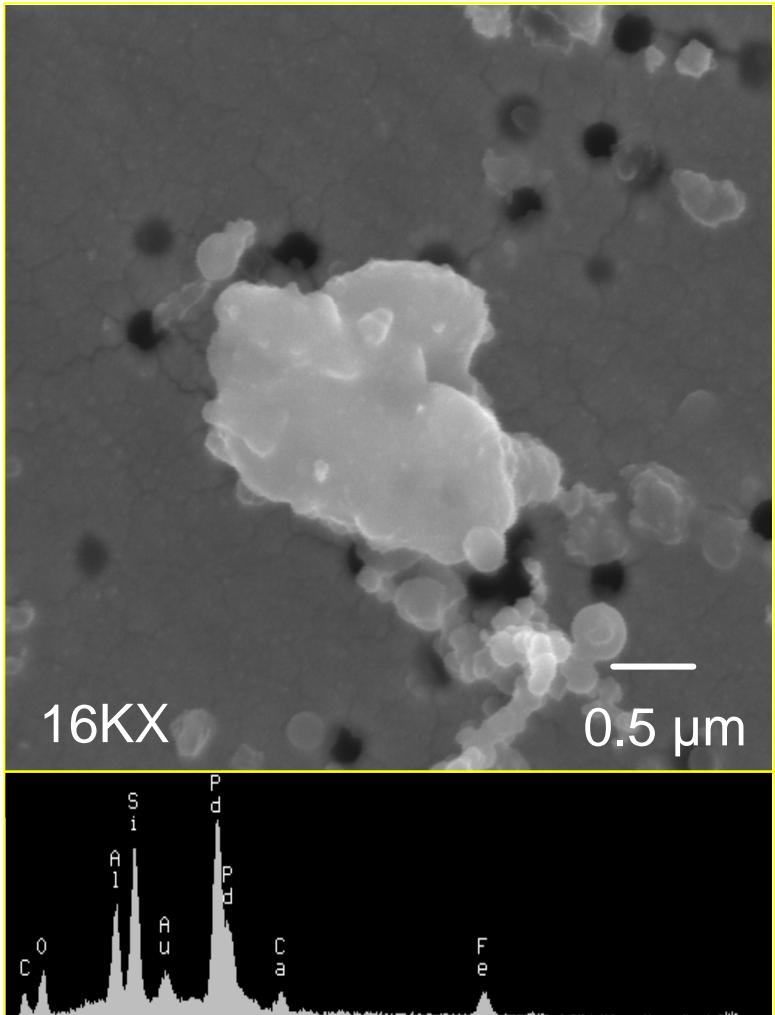
Secondary Electron Images

Carbon Chain Agglomerates



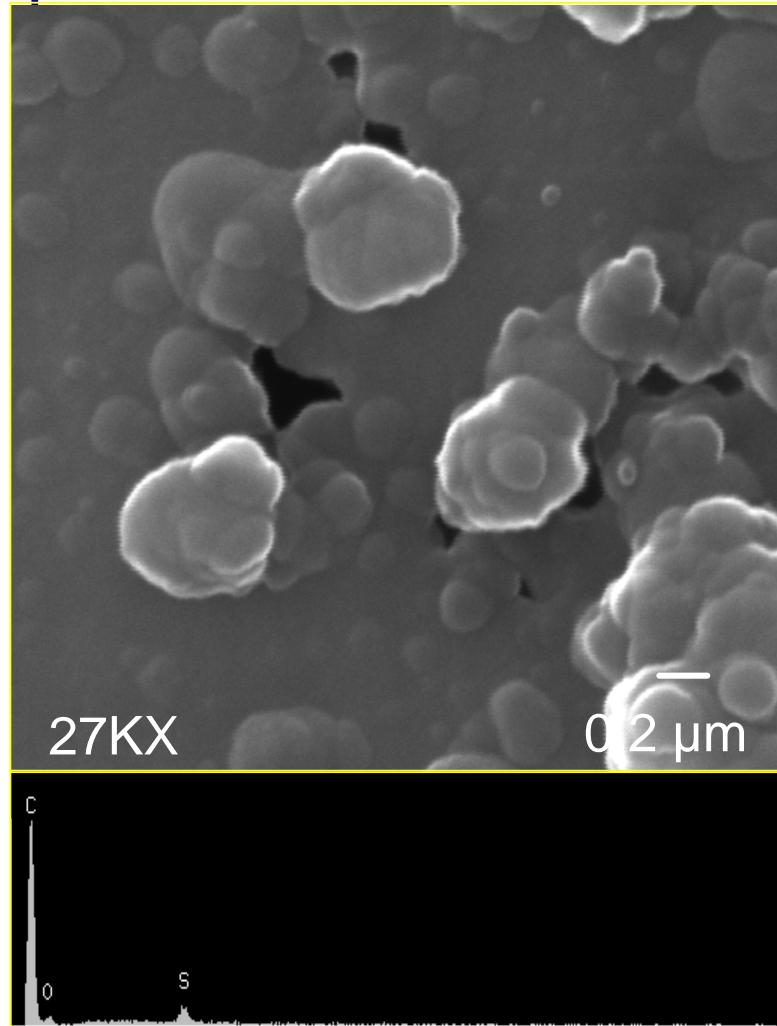
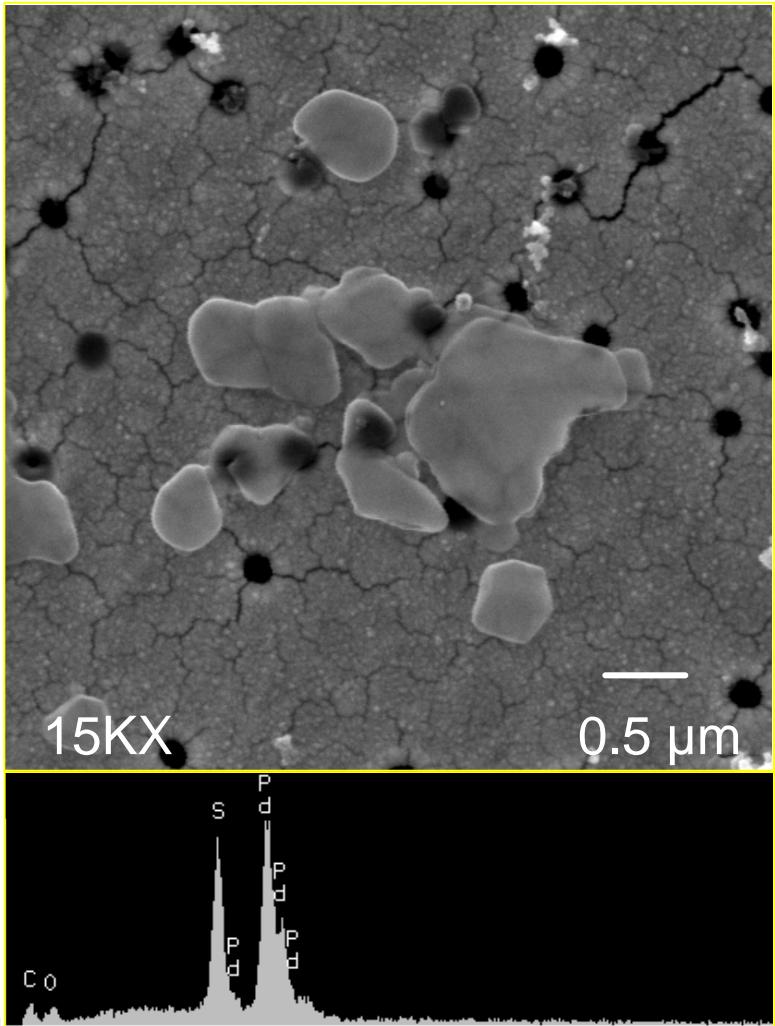
Secondary Electron Images

Crustal



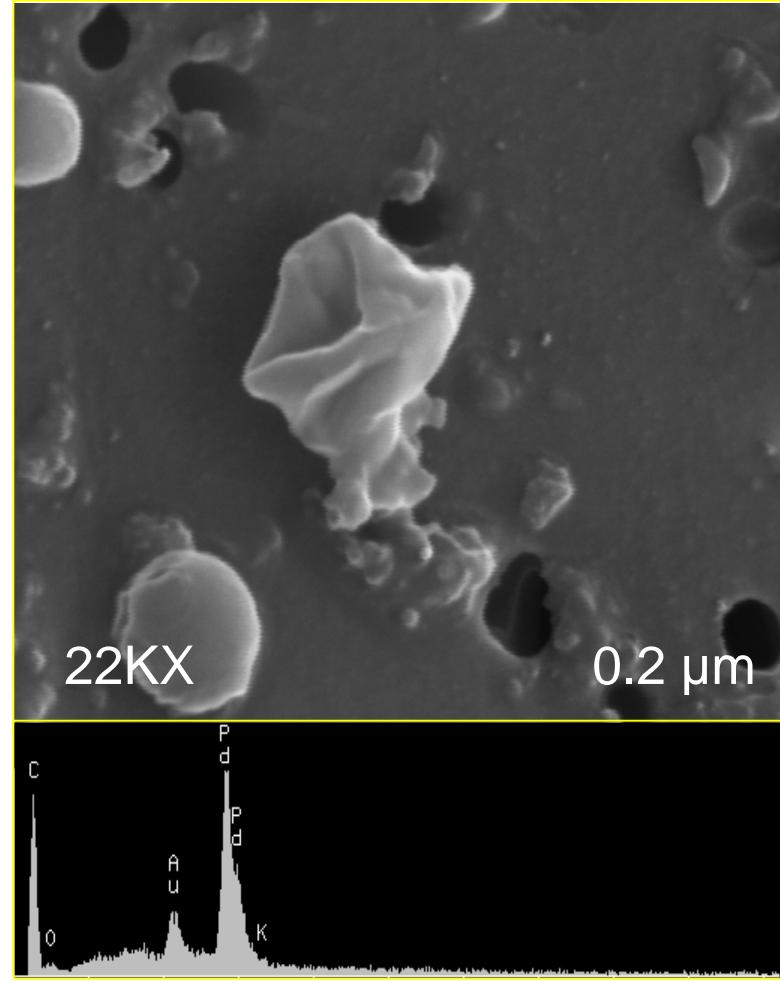
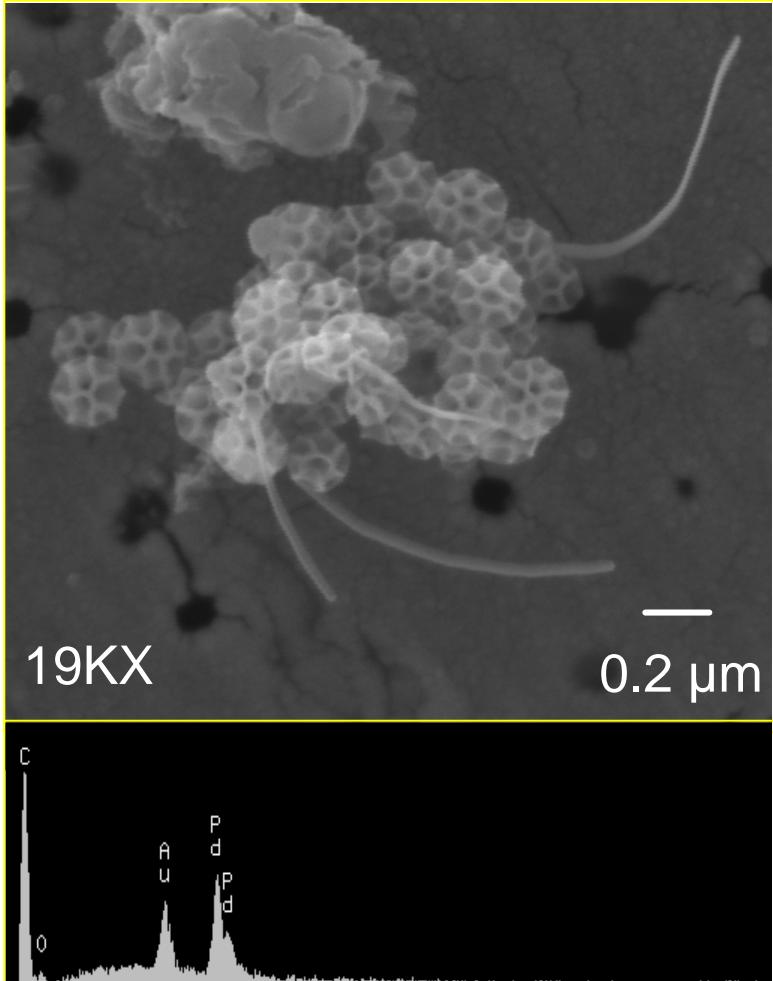
Secondary Electron Images

Sulfur Deposits

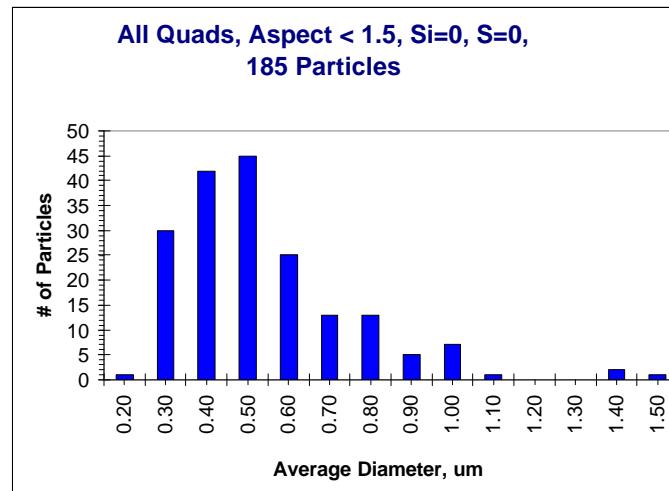
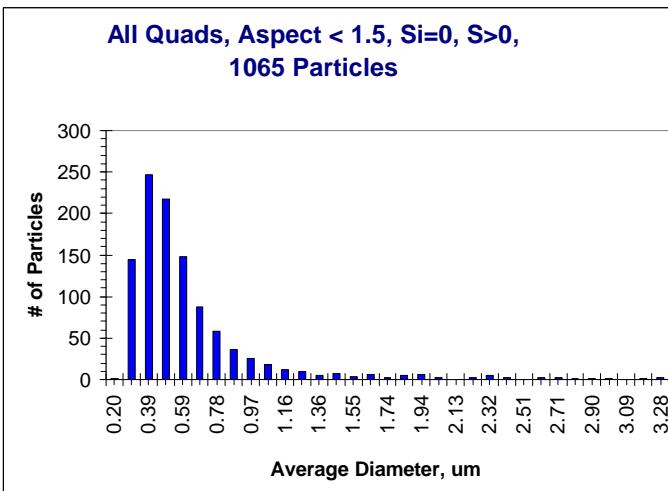
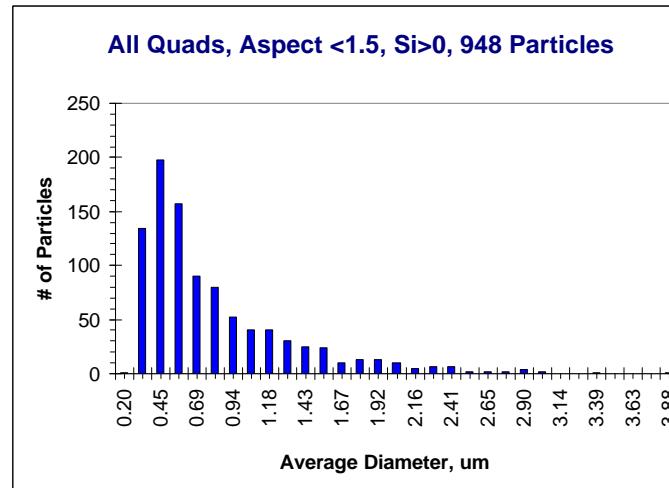
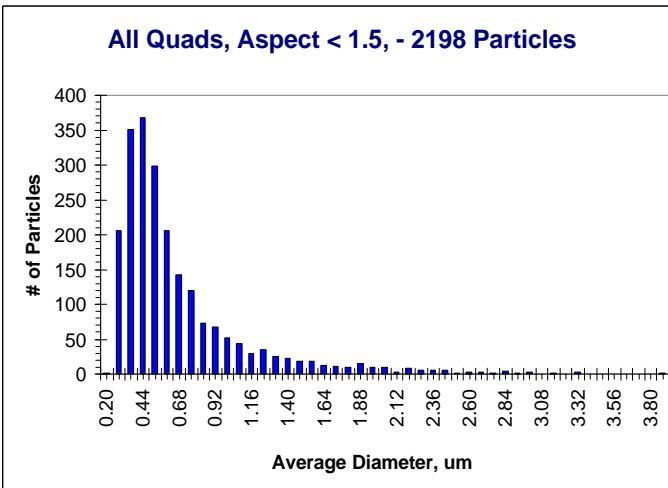


Secondary Electron Images

Plant Material



Distributions - Spherical Particles



From "Quantitative Scanning Electron Microscopy of Ambient Air 2.5 μ m Particles Using", *Air Quality II Conference*, McLean, Virginia, September 19-21, 2000.

Analysis Uncertainties

- Accounting for all sulfate particles in fields examined.
- Accurately estimating total sulfate particle volume.



Solution to Problem

- Normalize particle data to independently measured sulfate value



Analysis Results

FRM and SEM particle class data normalized to $\mu\text{g}/\text{m}^3$

Sample Start Date	24 Hour FRM $\mu\text{g}/\text{m}^3$	SEM Ammonium Sulfate	SEM Carbon Particles	SEM All Crustal Particle Types	SEM Spherical Alumino-Silicates	SEM Crustal	SEM Ca/S Rich	SEM Fe Rich Spheres	SEM Metal Oxide Particles	SEM Misc. Particles
08/06/00	20.8	9.77	5.97	5.06	0.87	3.79	0.30	0.06	0.02	0.03
08/08/00	23.4	13.95	4.93	4.51	0.24	3.67	0.51	0.00	0.01	0.07
08/10/00	15.7	7.94	6.34	1.37	0.03	0.92	0.00	0.09	0.30	0.03
08/12/00	7.6	2.08	3.57	1.95	0.09	1.10	0.07	0.09	0.39	0.21
08/14/00	17.8	9.07	6.20	2.53	0.08	2.04	0.03	0.22	0.15	0.01
08/16/00	9.5	4.76	2.72	2.02	0.26	0.60	0.67	0.00	0.37	0.13
08/18/00	14.0	8.17	3.66	2.17	0.07	1.17	0.41	0.22	0.24	0.07

FRM and SEM particle class data normalized to $\mu\text{g}/\text{m}^3$ (SEM particle class volume fraction x daily FRM). SEM data normalized to IC ammonium sulfate analysis. From "Quantitative Analysis of Ambient Air 2.5 μm Particles Using Scanning Electron Microscopy", 11th International Conference on Coal Science, San Francisco, Oct. 2001.

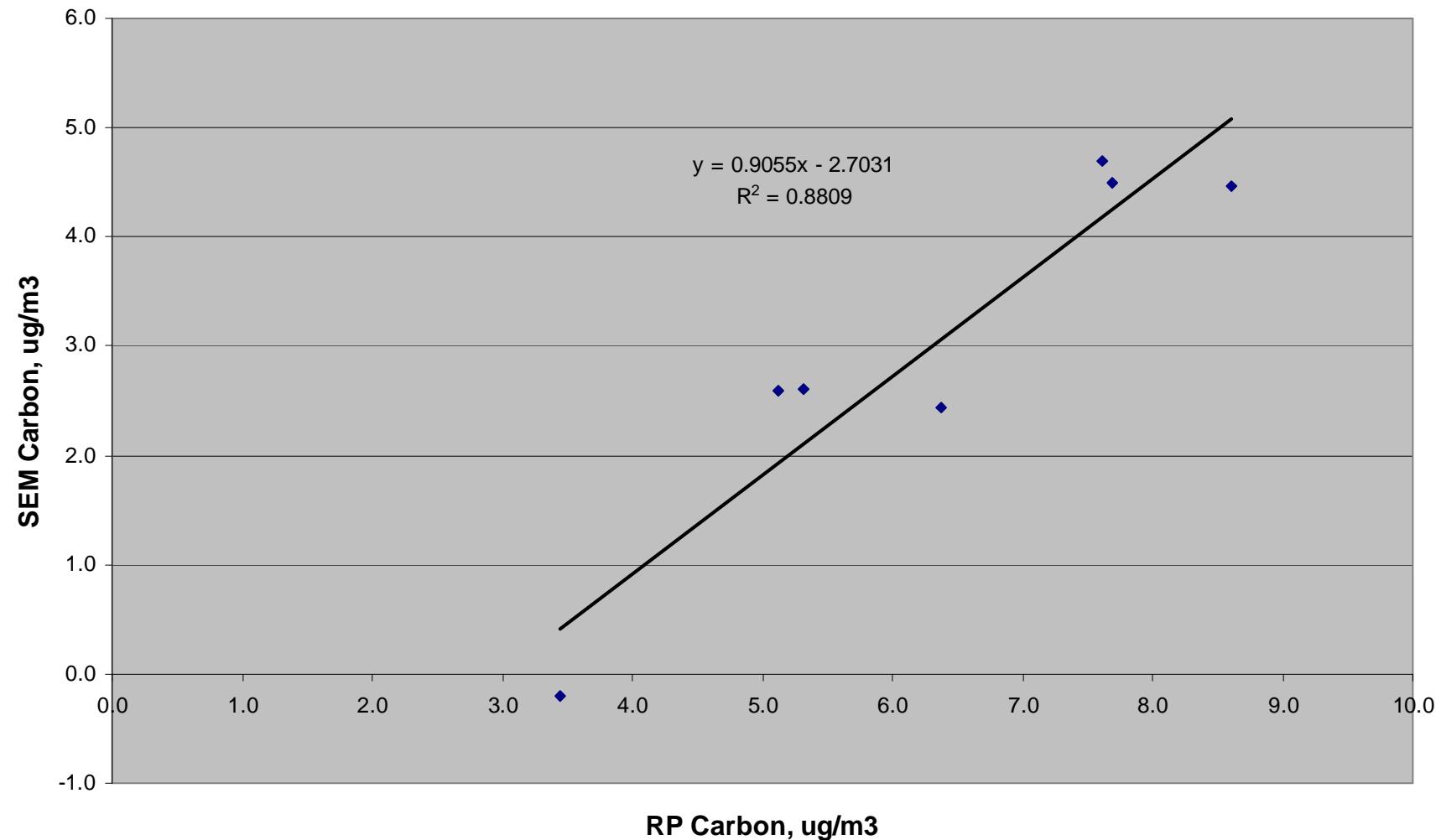


Verification of Experimental Approach

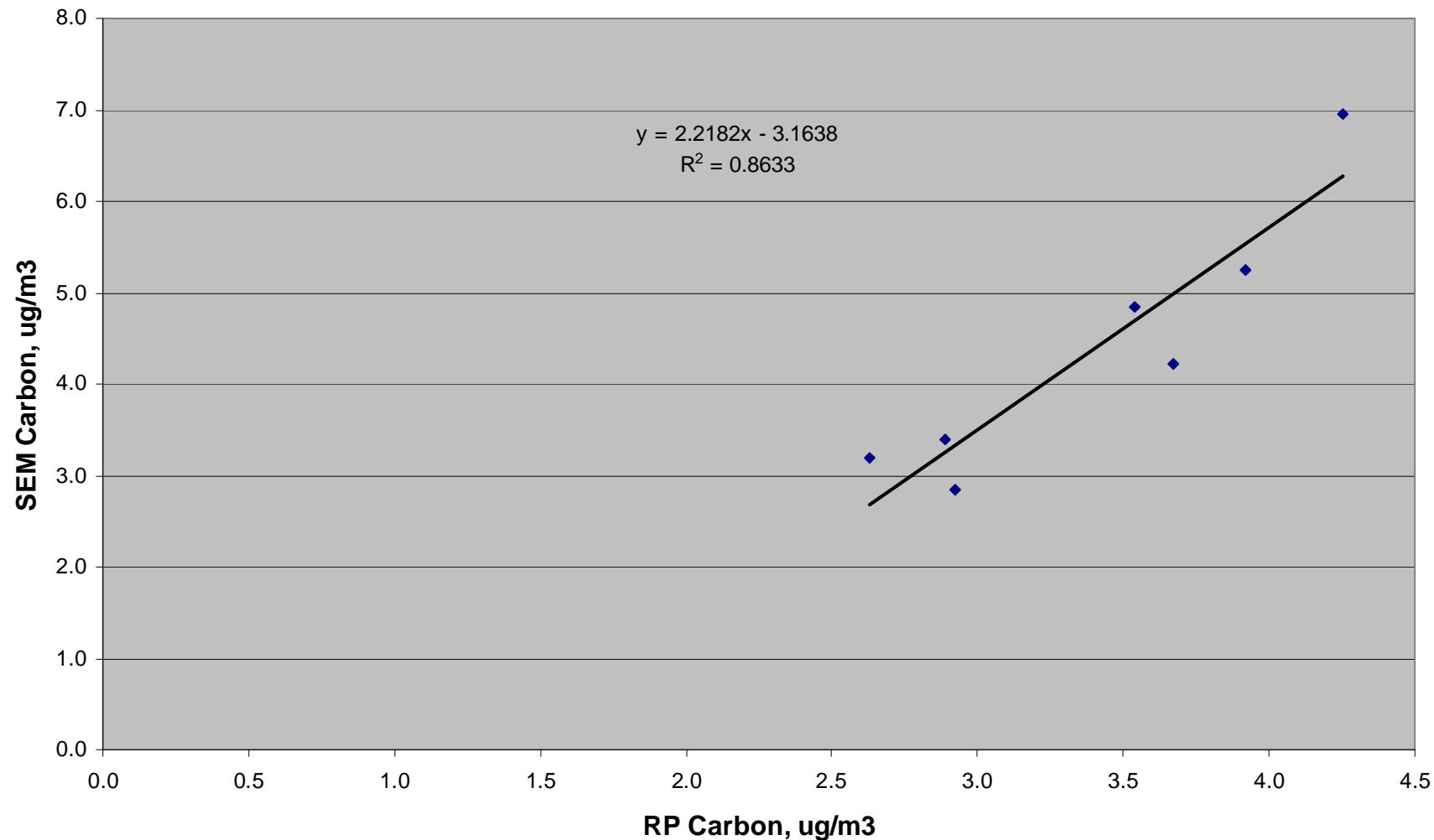
- Compare the adjusted values of next most abundant species (Carbon) with independently determined measurements



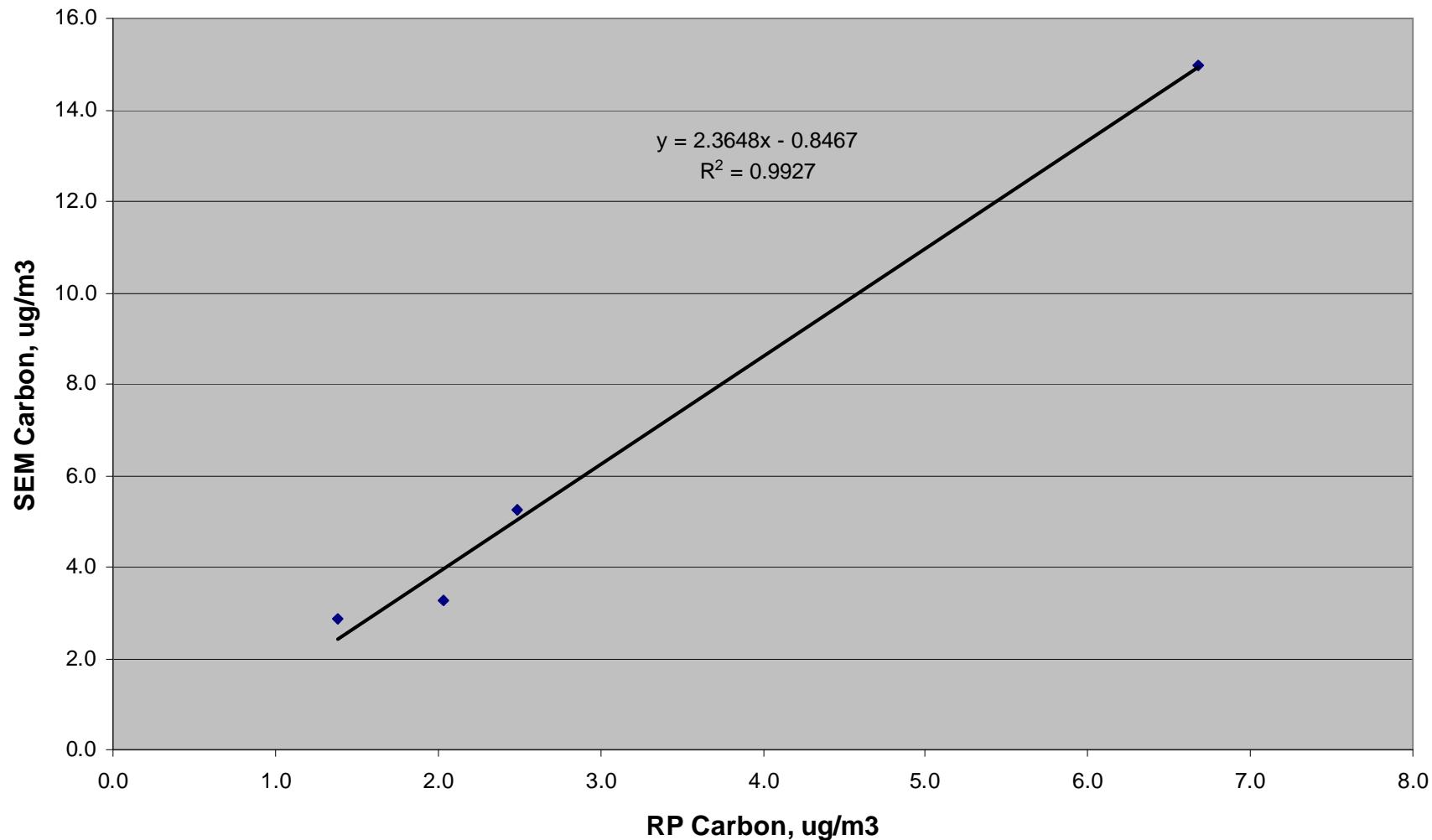
Spring 2000 RP Carbon vs. SEM Carbon



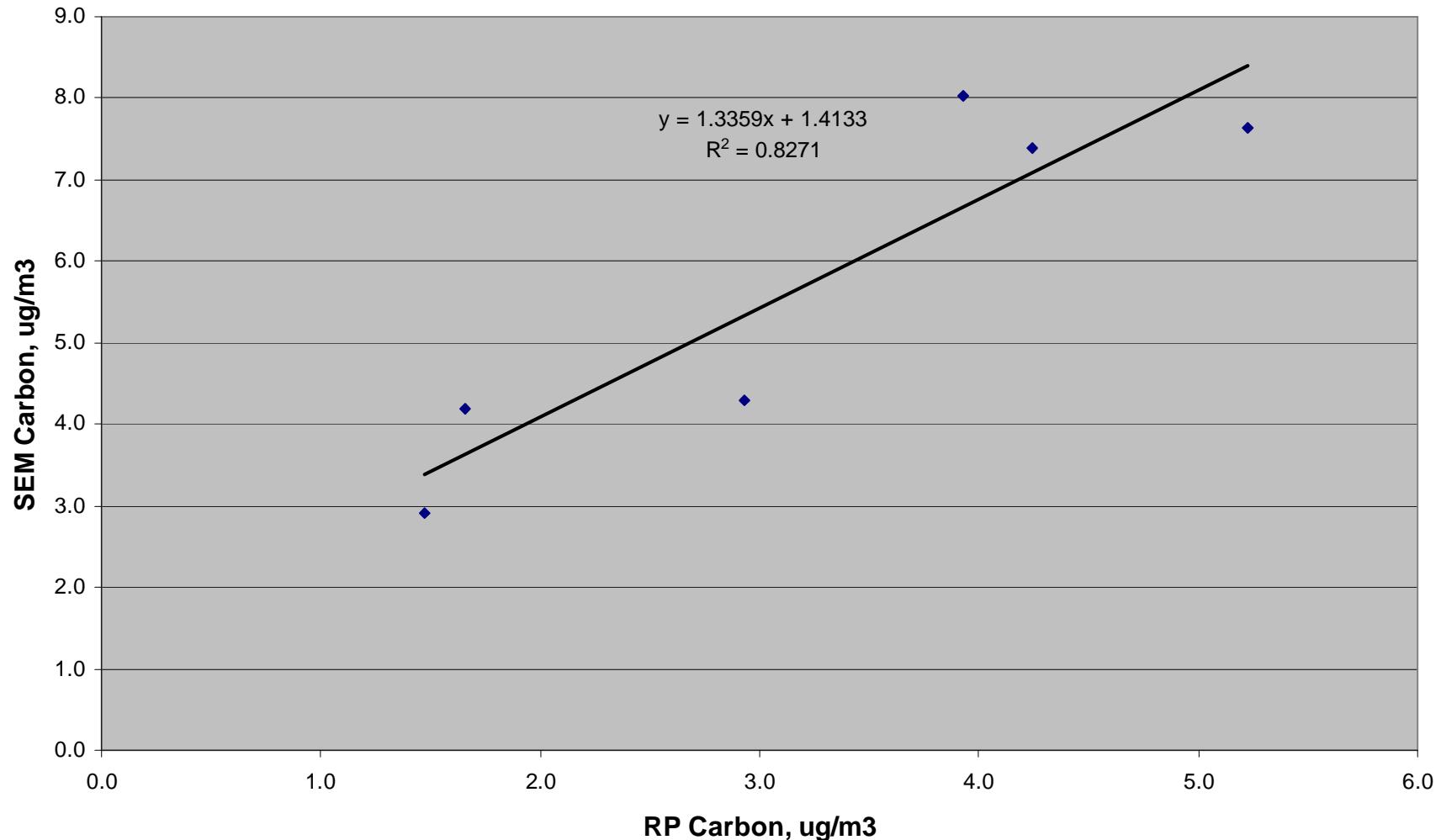
Summer 2000 RP Carbon vs. SEM Carbon



Autumn 2000 RP Carbon vs. SEM Carbon

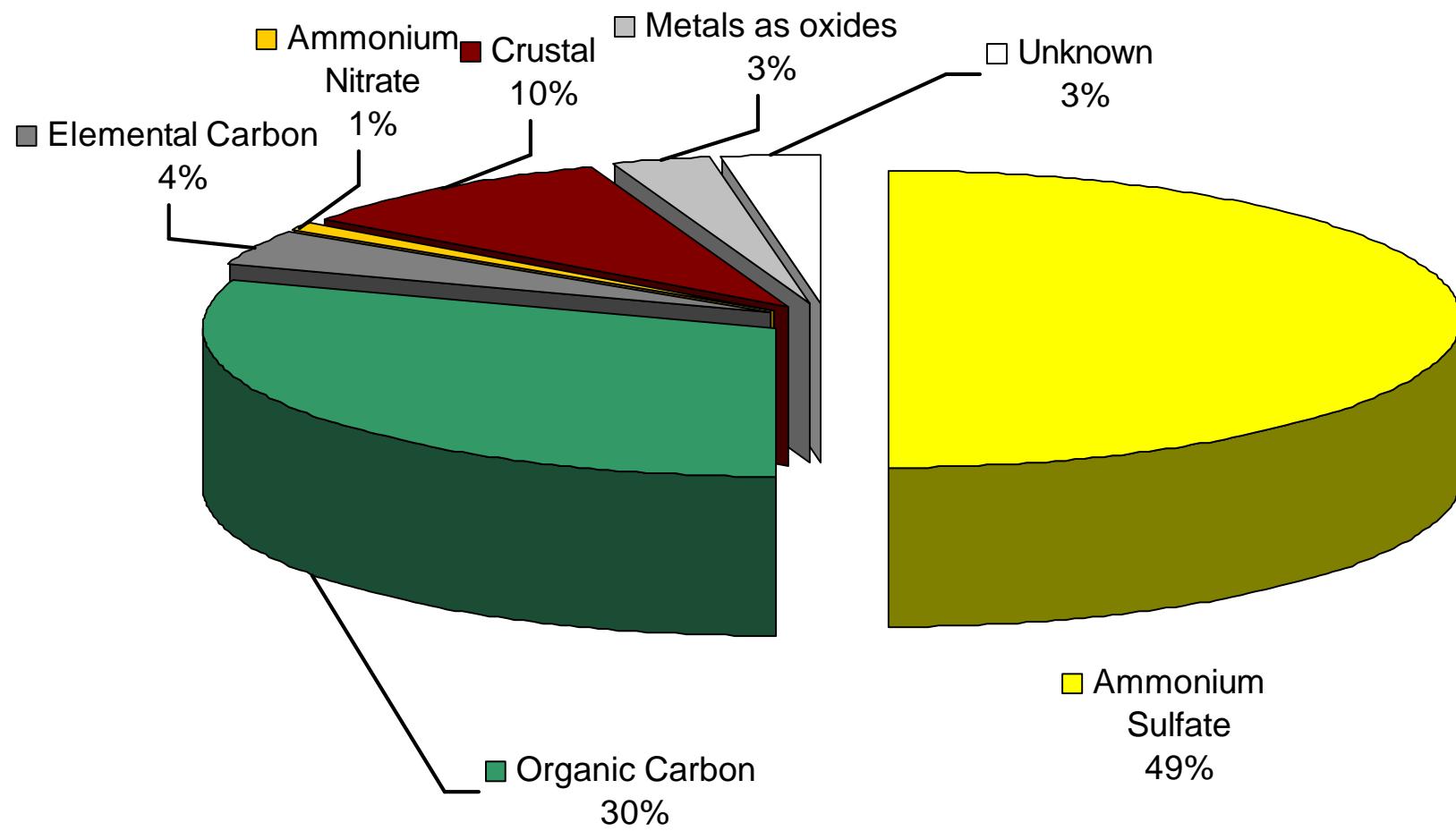


Winter 2001 RP Carbon vs. SEM Carbon

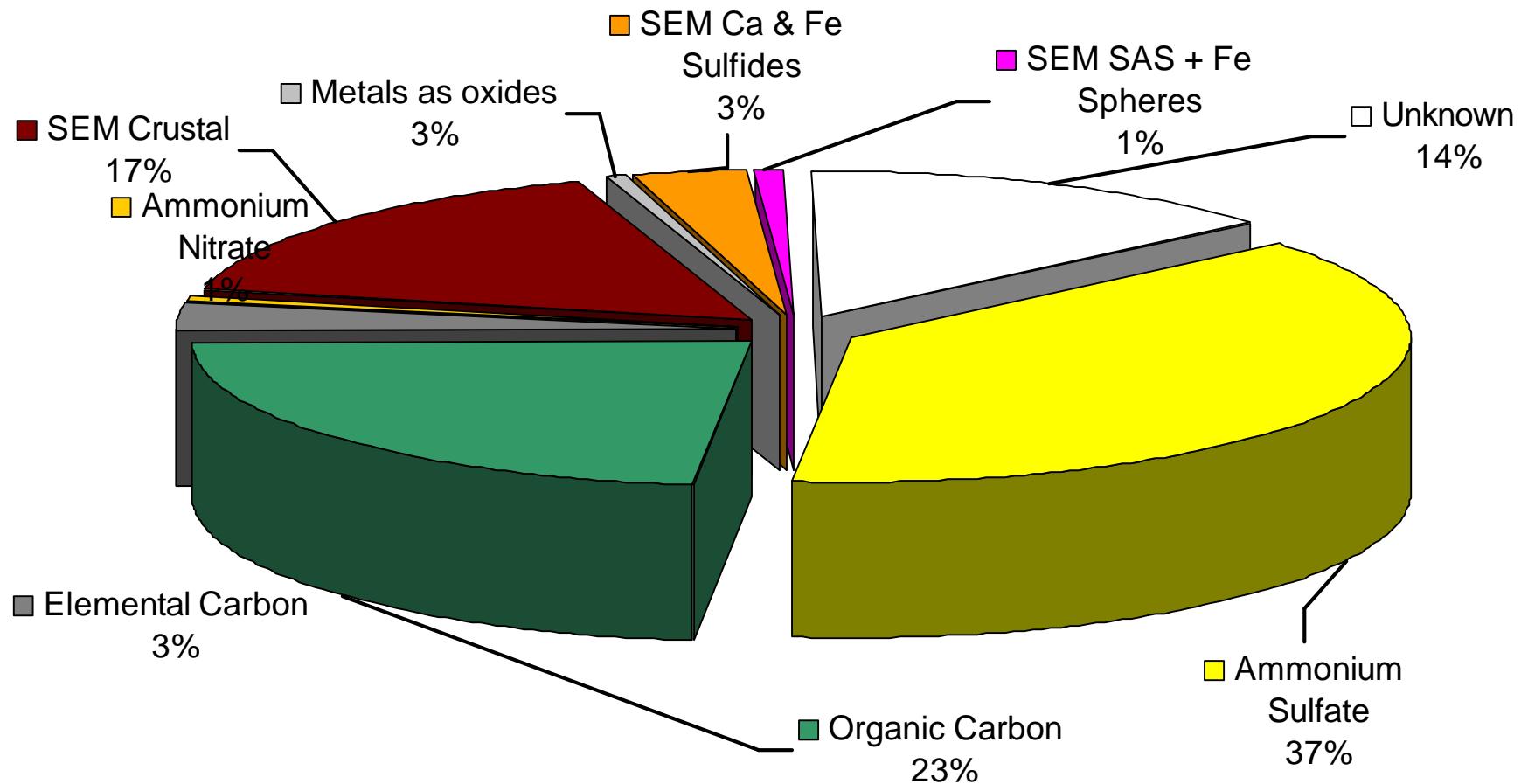


Results

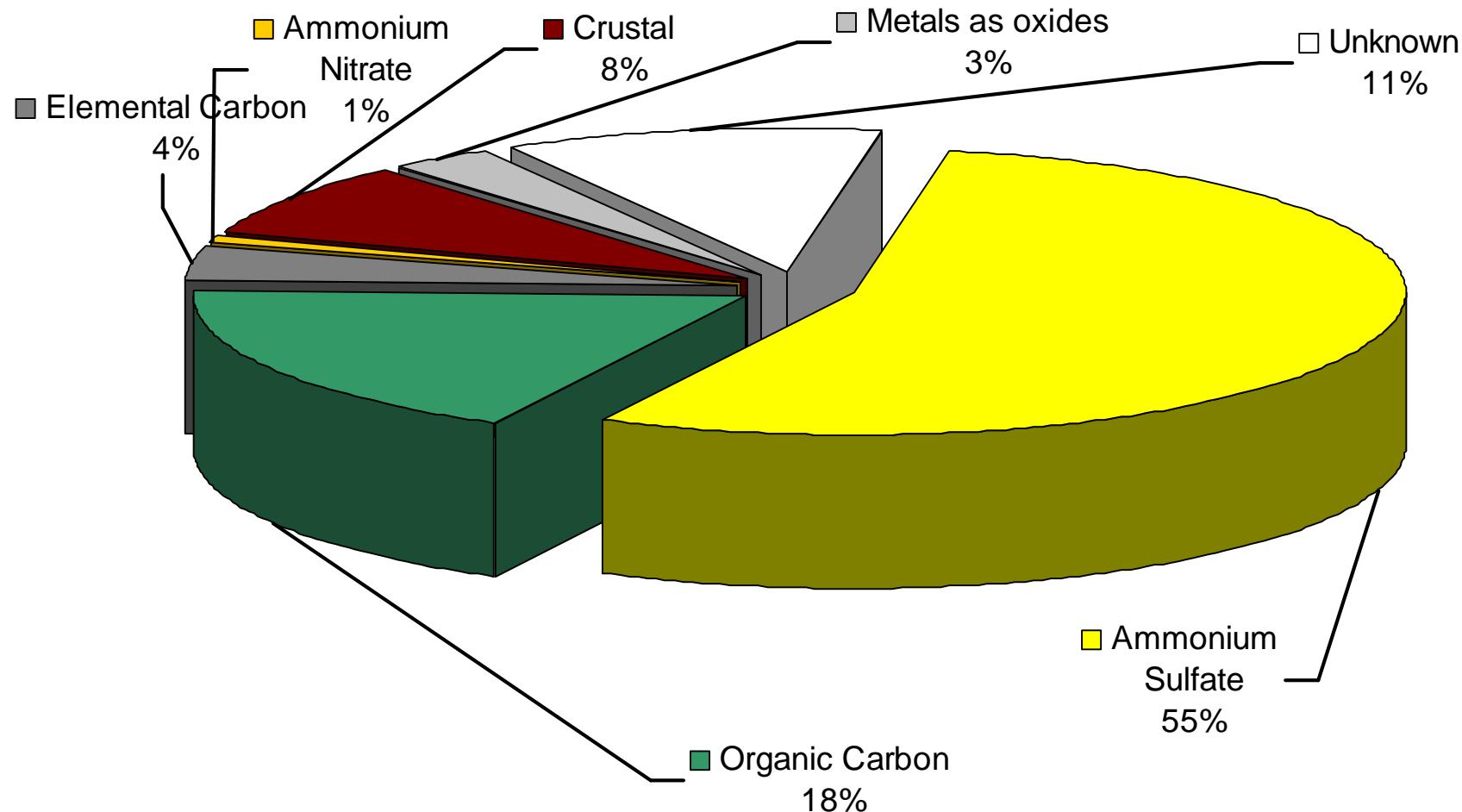
Spring 2000 Classic Data



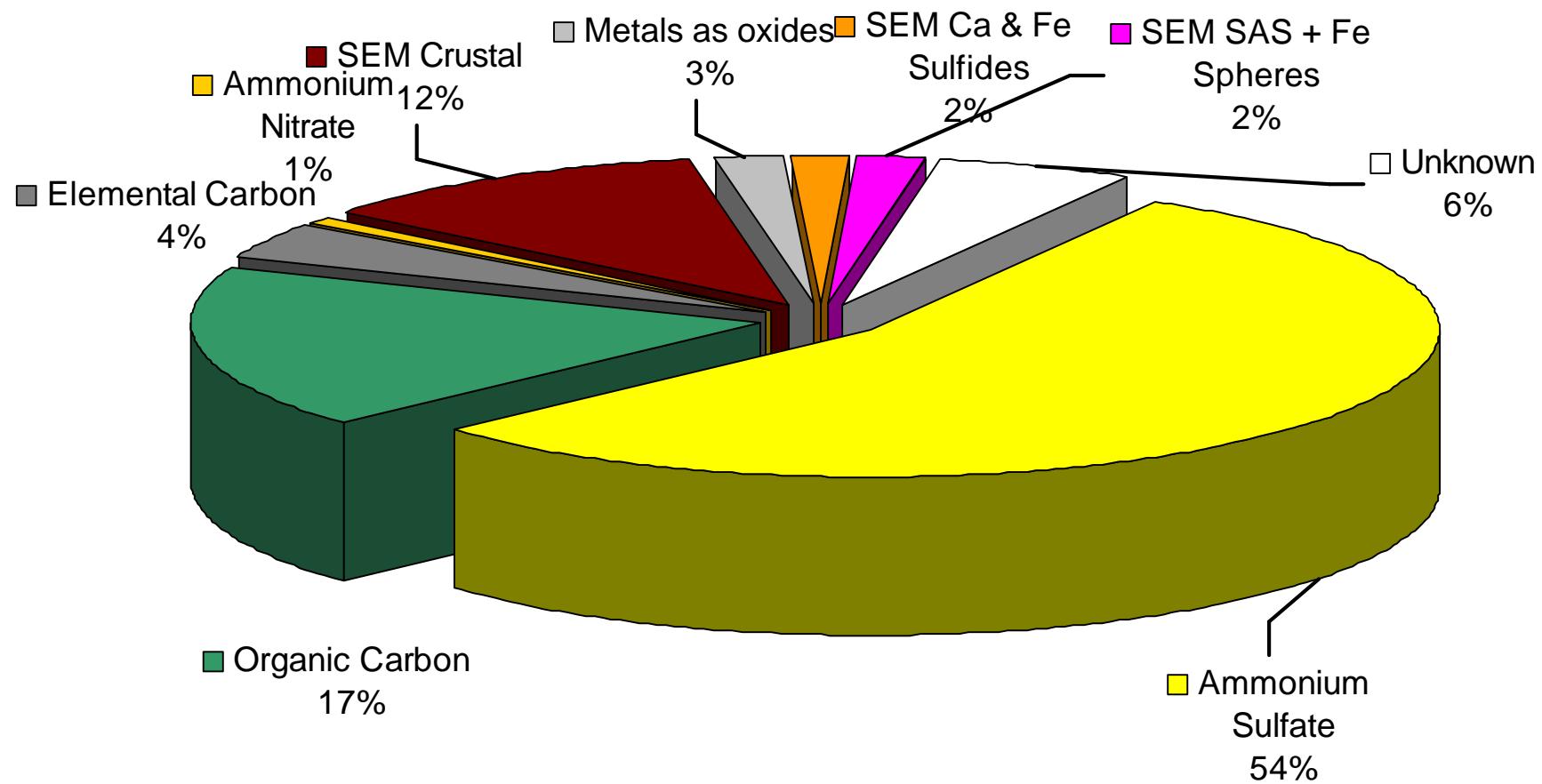
Spring 2000 SEM & Classic Data



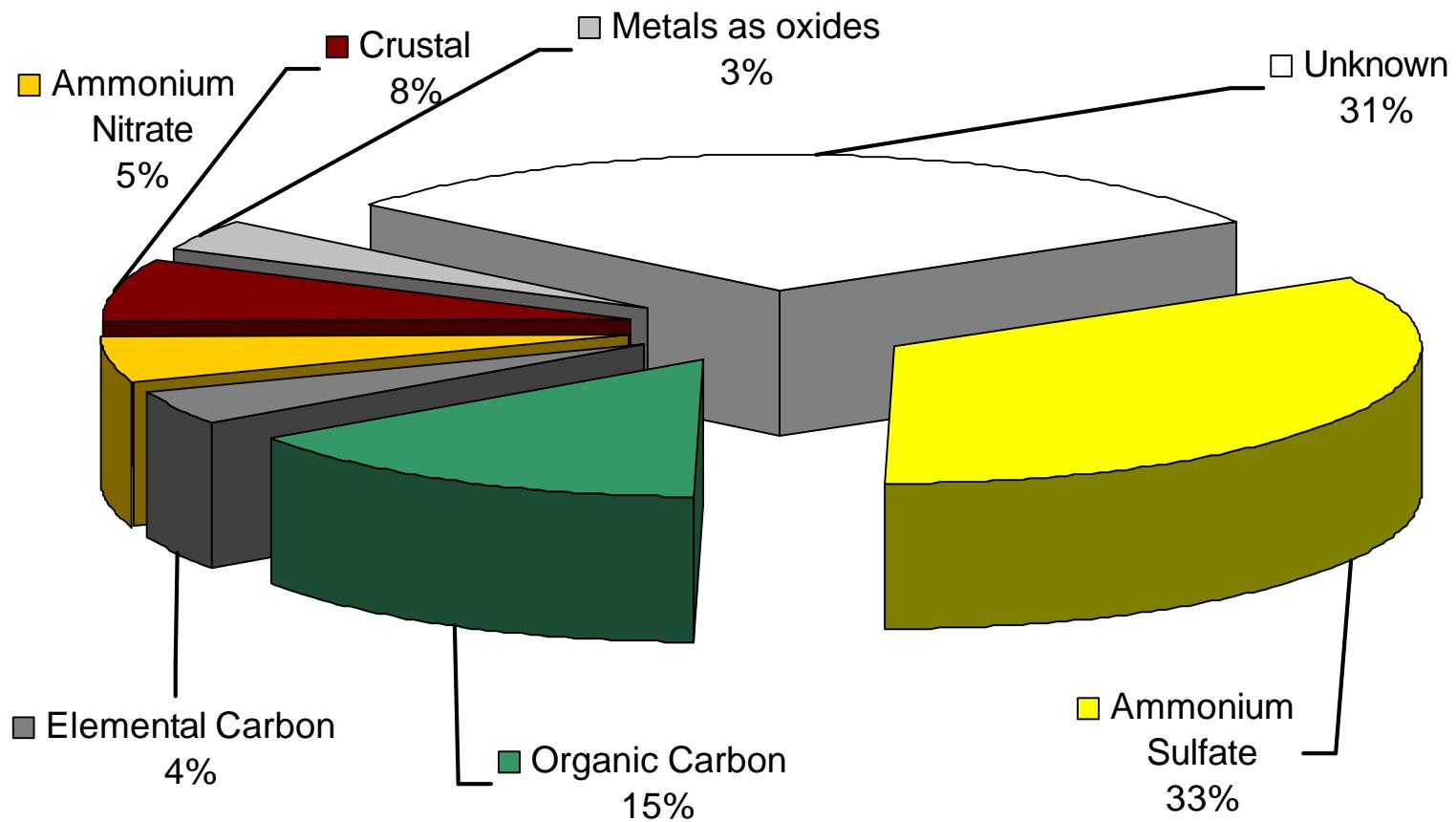
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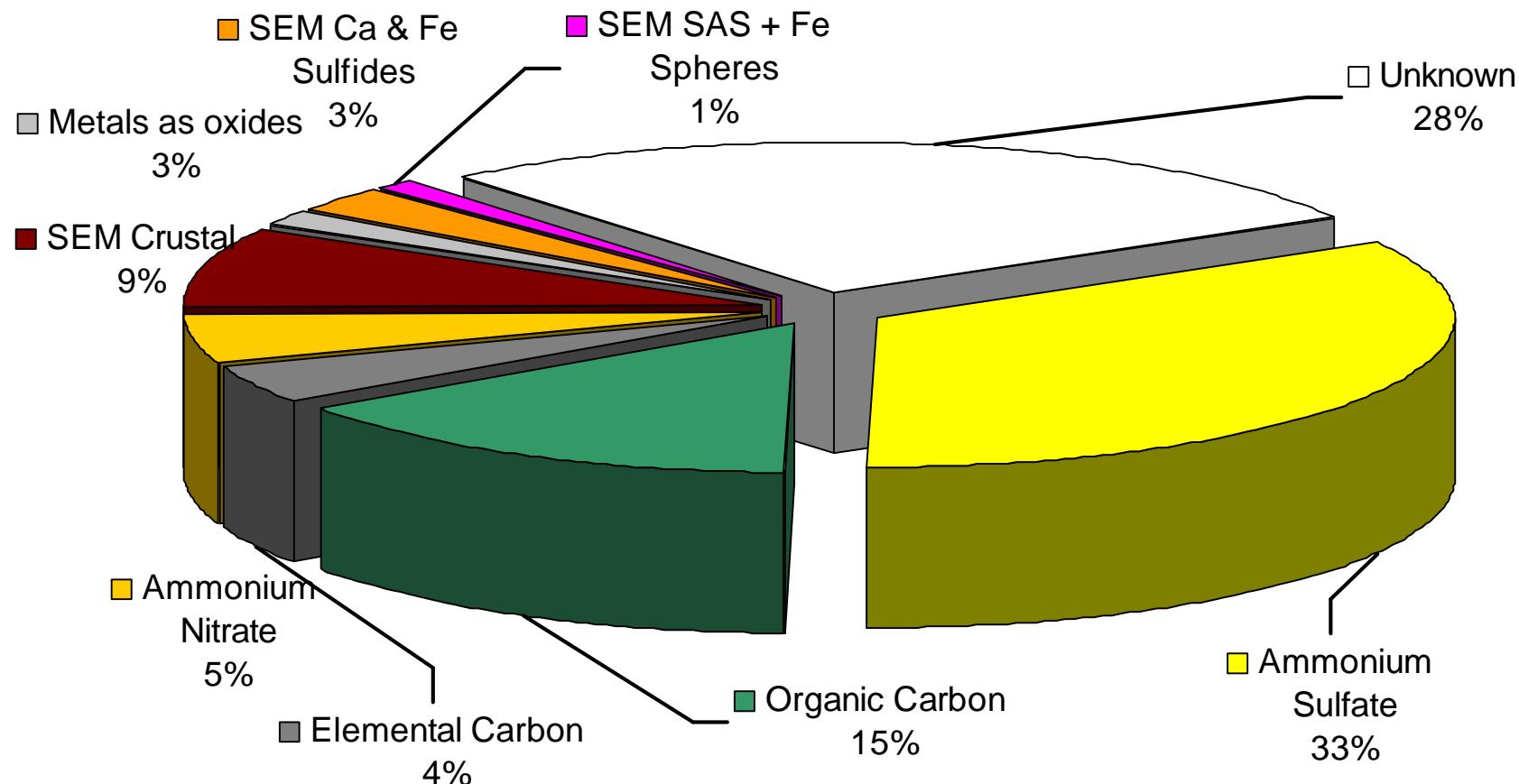
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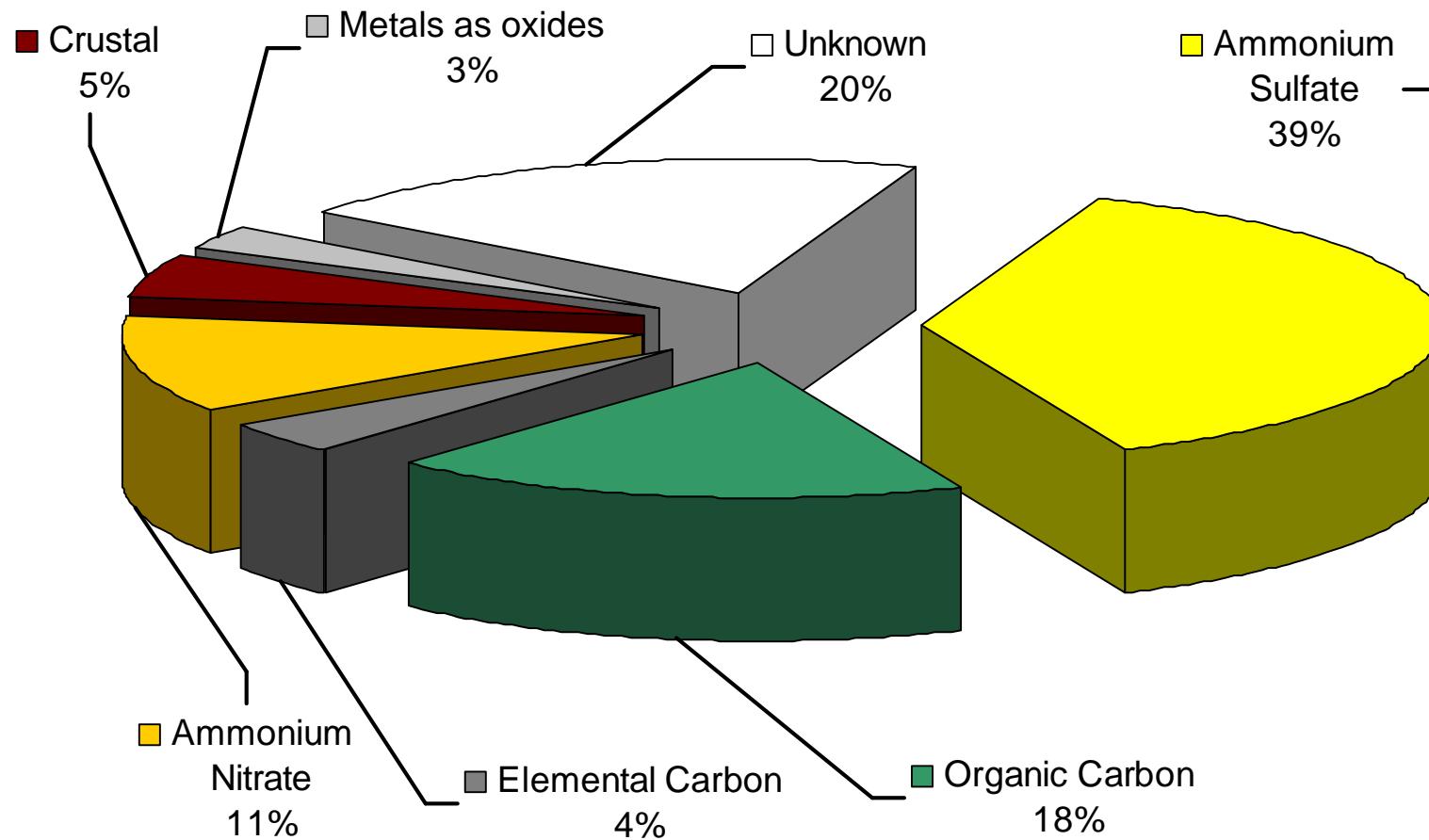
Autumn 2000 Classic Data



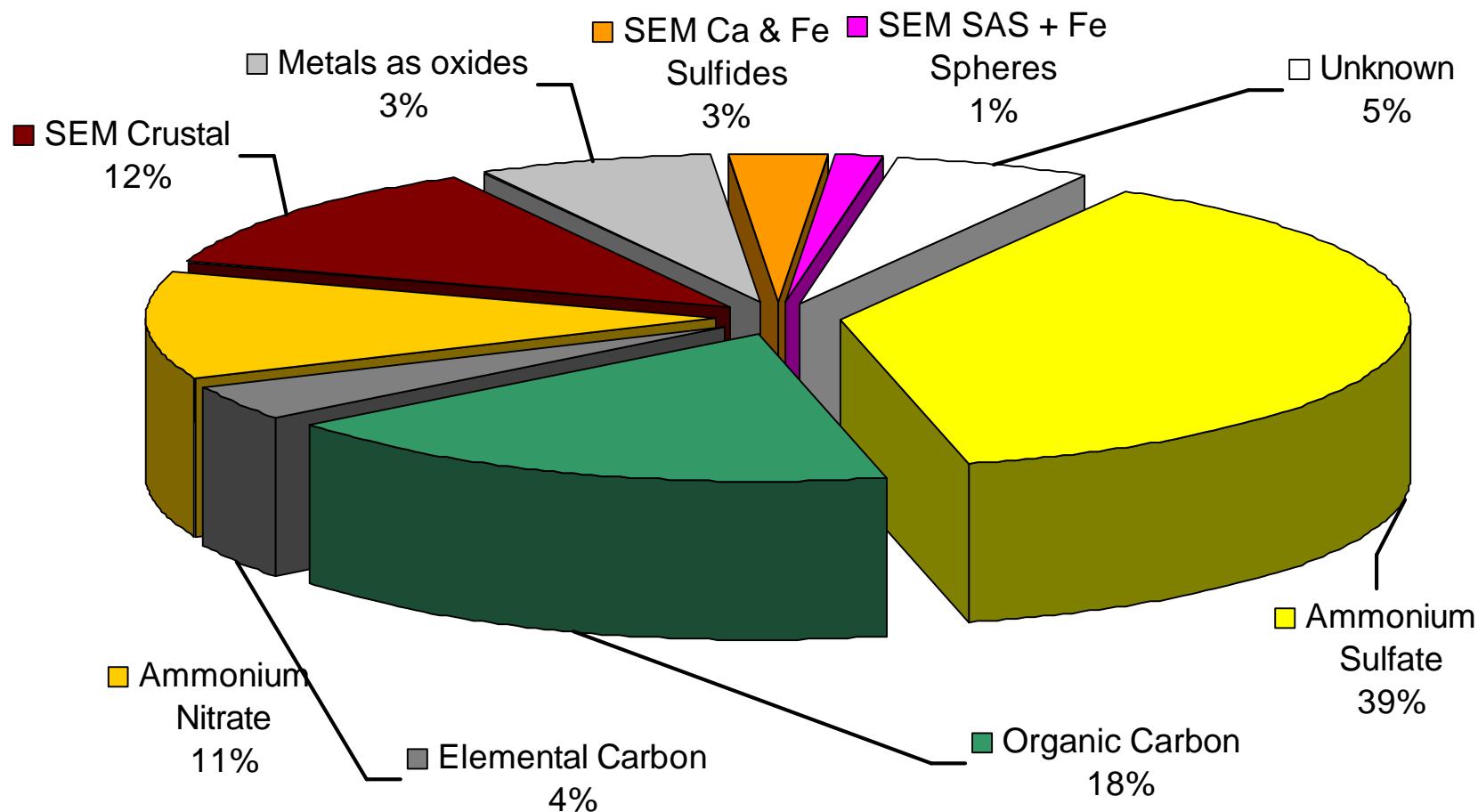
Autumn 2000 SEM & Classic Data



Winter 2001 Classic Data



Winter 2001 SEM & Classic Data



Results

- Additional information gained concerning amount of SAS (PCC primary particle source marker)
- Magnitude of ‘Unknown’ class is variable with both analysis approaches



Conclusions

- Sampling methodology is reasonably comparable to the FRM.
- The microscopy methods are of sufficient quality for comparative measurement of SAS particles.
- Further method refinements are required for direct comparison between SEM and all Classic analysis results.



Future Work

- Continue method refinements so that microscopy information can be used directly as a complement to, not a substitute for Classic analysis results.
- Utilize both particle size distribution and elemental chemistry information for generic source profiling.
- Enhance data on metal compound particle abundance for future health related studies.



Acknowledgments

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- The other PM_{2.5} Sampling and Analysis team members
- Mr. Thomas J. Feeley – Product Manager: Environmental and Water Resources, NETL

